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Enhanced emissions of NH_3, N_2O and H_2 from a Pd-only TWC and supported Pd model catalysts: Light-off and sulfur level studies

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ABSTRACT

In this work we study the formation of NH_3, N_2O and H_2 side products during operation of three-way catalytic converters (TWC) in a simulated engine exhaust. We used a commercial Pd-only TWC and supported Pd model catalysts in light-off and during constant temperature tests under rich conditions. N_2O is observed primarily during light-off and its low temperature formation (110–320 °C) proceeds via reduction of NO by CO when O_2 is present, or by H_2 in its absence. We detected also N_2O formation at 500 °C that has not been reported previously, proceeding via reduction with CO.

NH_3 is formed in the 200–600 °C range via reduction of NO by H_2. The H_2 required to produce NH_3 is generated via steam reforming and water gas-shift reactions over the catalysts. On a molar basis, the H_2 emission is about five-fold higher than that of NH_3 during cold start of TWC.

We determined the effect of SO_2 level during constant temperature experiments at 500 °C, extending the work of Gandhi and Shelef [1]. In CeO_2-containing catalysts the interaction with SO_2 favors the production of N_2O, but lowers that of NH_3, apparently by suppressing selectively the reaction path leading to H_2 needed for the reaction.

Our study suggests that the use of low and ultra-low sulfur gasoline by cars equipped with TWC lowers the emission of N_2O to the atmosphere during high temperature operation but enhances the production of NH_3 and H_2. This is a matter of concern because NH_3 is involved in the formation of nano, fine and ultra fine inorganic particles in the atmosphere.

1. Introduction

In an effort to improve the air quality in urban settings, the environmental regulations of several countries have put special interest in the removal of sulfur from gasoline and diesel fuels to lower emissions from mobile sources of SO_2, and of regulated compounds such as NO_x, CO and hydrocarbons [2]. As a result, there is a trend worldwide to produce high quality fuels with sulfur concentration as low as 2.5 ppmw. Besides, the direct impact upon acid rain and air quality, that measure aims at improving steadily the performance of the three-way catalytic converters (TWC), the main technology for control of regulated compounds emitted by cars [2–4].

Three-way converter technology is very dynamic, and formulations are continually being modified as a response to changes in engine technologies and gasoline composition. Nonetheless, it is possible to generalize their behavior based on the precious metal composition used. We have placed our attention on tri-metallic (Pt–Pd–Rh) and Pd-only systems in an attempt to cover the largest fraction of cars in operation, as well as the cars using newer technologies.

The number of vehicles equipped with Pd-only converters is increasing as the use of low-sulfur gasoline expands worldwide [5]. Pd-only TWC have excellent thermal stability and light-off performance, and are particularly effective in controlling hydrocarbons and CO. NOx conversion is equivalent or superior to the commercial rhodium/platinum-containing converters, and their cost is lower than bi- and tri-metallic TWC [6]. It appears that use of Pd-only TWC constitutes the best alternative to achieve the low CO, hydrocarbon and NOx emissions mandated for low emission vehicles (LEV), ultra low emission vehicles (ULEV) and super ultra low emission vehicles (SULEV) [7].

In spite of the TWC capability for transforming CO, HC and NO_x to CO_2, H_2O and N_2, the complex chemistry occurring during their operation includes several side reactions leading to as-yet unregulated compounds such as NH_3, N_2O and H_2 [8–12]. Reports about NH_3 and N_2O emissions from LEV, ULEV and SULEV vehicles have appeared recently [10,13–17], and results consistently show that NH_3 and N_2O emission rates are highest for the early catalyst technologies and decrease for more advanced technology vehicles. However, a close look at the issue indicates that there are still

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questions about the chemistry involved during light-off of the TWC, the effect of sulfur and the limit to emissions, particularly as attention is given to further lowering greenhouse gases, e.g. CO_2 and N_2O, and decreasing particulates in the atmosphere, an aspect where NH_3 plays a role.

The operation of the TWC is also affected by the presence of sulfur compounds in commercial gasoline. In fact, the use of low sulfur gasoline by cars equipped with TWC results in increased emissions of NH_3 [1,7,8,13,17,18]. For instance, Gandhi and Shelef [1] in a study of the effects of SO_2 on the performance of the noble metal catalysts reported that NH_3 formation is inhibited by SO_2 over Pt, Pd, Rh and Ir. They concluded that H_2 production via steam reforming (SR) and water gas-shift (WGS) reactions on the metals studied is inhibited in the presence of SO_2, and hence NH_3. However, they did not study the formation of H_2 and N_2O in their catalytic tests.

In this work, we study the formation of NH_3, N_2O and H_2 over a commercial Pd-only TWC and supported $Pd/CeO_2–Al_2O_3$ model catalysts using a simulated engine exhaust under rich conditions. We also study the effect of sulfur content upon formation of those compounds at constant temperature (500 °C) and find how the selectivity towards NH_3 and N_2O depends on the sulfur content and ceria content. We also discuss the unexpected formation of N_2O at 500 °C.

2. Experimental

2.1. Catalysts preparation

We used as a reference a fresh commercial TWC labeled Pd-only TWC (Peasa L. Tech., model 2000 EX series for Nissan vehicles, PIREC program in México City) with 400 cells per square inch. Model catalysts were prepared by wet impregnation with a solution of $Pd(NH_3)_4(NO_3)_2$. Pd/Al_2O_3 and $Pd/CeO_2–Al_2O_3$ model catalysts containing 10 wt.% of CeO_2 were used in the catalytic test. Commercial γ-Al_2O_3 (Aldrich) was crushed/sieved to 120–140 mesh. CeO_2 was prepared by thermal decomposition of $Ce(NO_3)_3·6H_2O$ at 800 °C during 4 h. The addition of ceria to the alumina was by wet impregnation. $CeO_2–Al_2O_3$ was dried at 115 °C for 4 h and calcined at 800 °C for 8 h before impregnation with 0.4 wt.% of Pd. The materials were then dried for 4 h at 120 °C and then calcined for 12 h.

2.2. Catalytic tests

Catalysts were tested in a tubular quartz reactor mounted in a temperature-programmed electric furnace (Chromalox 2104). A porous quartz frit disk was placed in the middle of the tube to hold the materials. In the case of the commercial converter, we cut a 16 channel (4 × 4) monolith sample with a volume of 0.562 cm^3 (solid plus void volume). In the case of the model catalysts we used 100 mg samples. The total amount of Pd present in the reactor was the same in all cases. The catalysts were pretreated at 600 °C for 2 h under flow of 100 cm^3/min of N_2.

Six flow controllers were used to measure flow rates of NO + N_2, C_3H_8 + N_2, CO + H_2 + N_2, O_2 + N_2, SO_2 + N_2 and N_2. Certified standard N_2 and gas mixtures were purchased from Infra and Praxair (México). H_2O was delivered by a syringe pump and it was vaporized in heated lines before reaching the reactor.

During the light-off tests and for the constant temperature experiments with the Pd-only TWC, the feed stream contained 2100 ppm of NO, 2200 ppm of H_2, 6600 ppm of CO, 515 ppm of C_3H_8, 5300 ppm O_2 and 10% by volume of H_2O in N_2. SO_2 ranged from 0 to 20 ppm. Rich mixtures were prepared by adjusting the oxygen concentration to obtain the equivalent of an Air to Fuel (A/F) ratio of 14.6% (w/w). In the case of constant temperature runs at 500 °C with

Table 1
Textural characteristics of model catalysts.

Catalyst[a]	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (nm)
Pd/Al_2O_3	186.5	0.48	10.3
$Pd/2-CeO_2–Al_2O_3$	165.8	0.40	9.8
$Pd/10-CeO_2–Al_2O_3$	162.9	0.43	10.6

[a] The number in the code means the wt.% of CeO_2.

the model catalysts, the feed stream composition was 2100 ppm of NO, 2200 ppm of H_2, 6600 ppm of CO and 20 ppm SO_2. In all cases, N_2 was the gas balance and the total flow was 950 cm^3/min. The space velocity was 100,000 h^{-1} for Pd-only TWC.

The analysis of reactants and products was made on-line by means of a NO_x detector (Rosemount 951 A) and gas chromatography (GC) (HP 6890 equipped with a H Plot Q column) was used to detect C_3H_8, and a Shimadzu 12A GC equipped with a molecular Sieve 5A column was used to detect H_2, CO and O_2. An FTIR spectrophotometer (Bruker Tensor 27 equipped with a 0.75 m path-length gas-cell heated to 120 °C to prevent condensation) was employed on-line to detect NH_3 and N_2O. Spectra were acquired at a 4 cm^{-1} resolution by averaging 44 scans.

During light-off runs the temperature of the reactor was raised from 25 to 600 °C at 2 °C/min. In the case of constant temperature experiments (at 500 °C), the reactor was heated at 8 °C/min from room temperature up to 500 °C in a flow of 100 cm^3/min of N_2 and stabilized for 1 h prior to the measurements.

2.3. Catalyst characterization

The Pd loading of the TWC, determined by atomic absorption, was 2.3×10^{-4} g/cm^3, and the washcoat composition, measured by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) (JEOL, JSM-5900), was 23.8 wt.% of Al_2O_3, 2.6 wt.% of CeO_2 and 0.6 wt.% of BaO (on a total monolith weight basis).

Textural characteristics of Pd/Al_2O_3, $Pd/2-CeO_2–Al_2O_3$ and $Pd/10-CeO_2–Al_2O_3$ were obtained by nitrogen physisorption (Autosorb, Quantachrome). Specific surface area (S_{BET}) was estimated from nitrogen isotherms. Pore-size distributions (PSD) were calculated from the desorption branch of the nitrogen isotherms according to Barrett, Joyner and Halenda (BJH method). Samples were degassed at 100 °C under vacuum for 24 h prior to the characterization.

3. Results and discussion

3.1. Textural characteristics

Table 1 shows textural characteristics of the model catalysts. There are no significant variations in porosity and surface area of the parent Al_2O_3 once the presence of CeO_2 is accounted for. In this case ceria does not act as a textural promoter.

3.2. Light-off operation under rich conditions

3.2.1. Pd-only TWC

As the TWC lights-off, NO is reduced to N_2, N_2O and NH_3. The proportion of the secondary products, N_2O and NH_3, is a strong function of the temperature, the A/F ratio and the sulphur content. The formation of N_2O and NH_3 over Pd-only TWC is presented in Fig. 1. Our results indicate that under rich conditions NO reduction to N_2O occurs in the commercial TWC via reaction with CO at low temperature (from 110 to 320 °C). This is within the range reported for cars under standard driving conditions, as N_2O is released primarily as a spike upon starting the engine, observed roughly

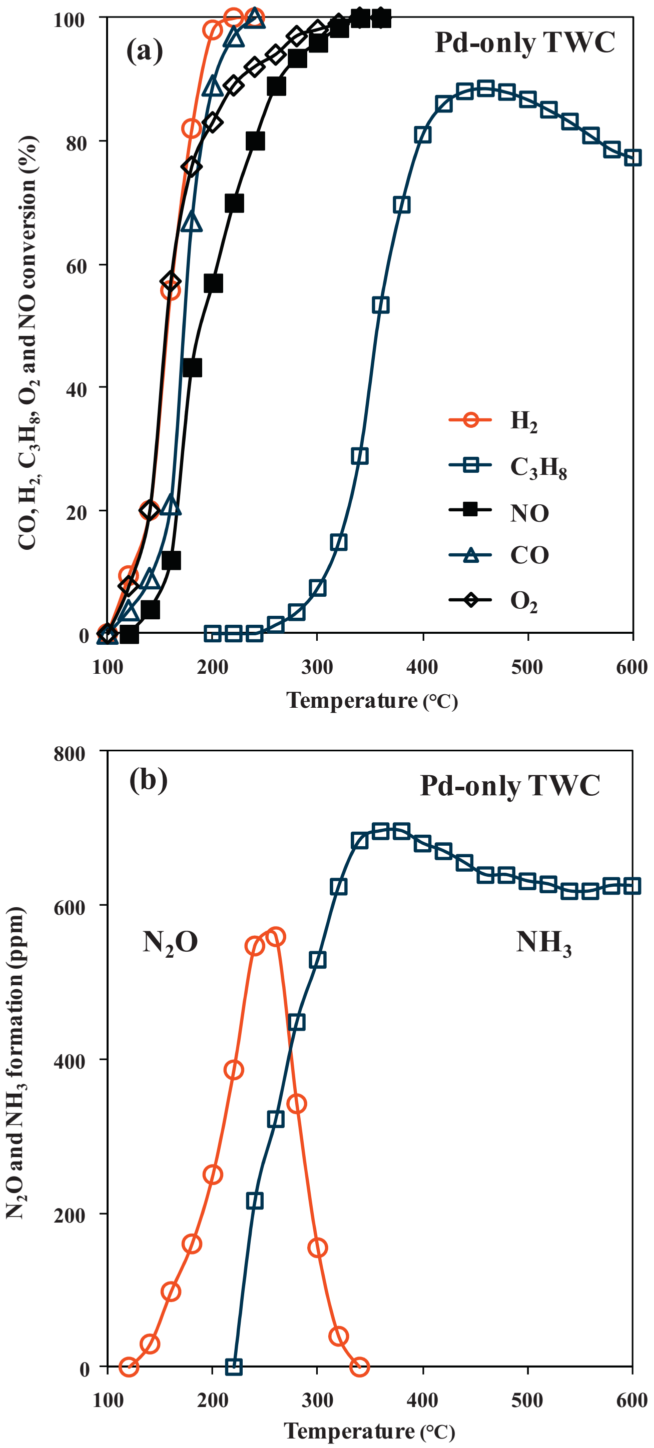

Fig. 1. (a) NO, CO, H_2, C_3H_8 and O_2 conversion as a function of the temperature and (b) N_2O and NH_3 formation over commercial Pd-only TWC during light-off as a function of the temperature. Rich conditions – 2100 ppm of NO, 515 ppm of C_3H_8, 2200 ppm of H_2, 6600 ppm of CO, 10% (v/v) of H_2O and 0.53% by volume of O_2. A/F = 14.60.

between 250 and 450 °C [11,15]. Our experimental method allows us to broaden the spike and analyze closely the yield-temperature behavior in contrast to the analyses in cars, where the heating rate is of the order of 100 °C/min and measurement time lags affect the observations.

NH_3 is formed beginning above 210 °C, in this case by reduction of NO by H_2. In the 200–300 °C range most of the NO reduction products are N_2O and NH_3. At about 250 °C almost 90% of the NO reduced transforms to N_2O and NH_3. NH_3 is the main side product as the temperature of the TWC is raised above 300 °C.

To further understand the network of reactions involved in the production of NH_3 and N_2O on the TWC, we performed experiments with the Pd-only TWC using different feed streams. Fig. 2(a) shows the reactions of the NO + C_3H_8 + O_2 mixture. The hydrocarbon and oxygen start reacting at about 300 °C. H_2 and CO are formed when O_2 is nearly depleted, above 400 °C. The presence of H_2 correlates with the production of NH_3 via reduction of NO. N_2O is not detected in this case.

When the feed consists of NO + CO + H_2 and NO + CO + H_2 + H_2O the yield-temperature pattern for the production of N_2O and NH_3, given respectively in Fig. 2(b) and (c), is similar to the one observed with the simulated engine exhaust (Fig. 1). A large N_2O spike is observed between 100 and 310 °C, produced by reaction of NO with H_2, whereas NH_3 forms at roughly 250 °C and levels off after 350 °C. To summarize, in the absence of O_2, the reduction of NO is with H_2. There are slight variations in the yield-temperature curves depending on the feed stream composition, but that is not surprising, given the complexity of the reaction network.

To verify the origin of the H_2 required to produce NH_3, both steam reforming and water gas shift reactions were performed with the TWC. Results are given in Fig. 3. SR is activated at about 250 °C, whereas WGS begins roughly at 320 °C. These results confirm the possibility of generating H_2 at high temperatures in the TWC. NH_3 can be observed beginning at about 220 °C during our simulated exhaust light-off experiments because C_3H_8 SR is being activated at that temperature. At higher temperatures WGS becomes relevant too.

The emission of N_2O and NH_3 observed in our experiments is in agreement with measurements of these compounds from vehicles [11,15]. For instance, Huai et al. [15] reported N_2O formation during catalyst light-off between 250 and 450 °C on vehicles. Heeb et al. [16] detected the presence of NH_3 at temperatures between 242 and 625 °C for a transient urban driving cycle. The presence of H_2 is key to understanding the formation of N_2O and NH_3 from TWC in cars. Heeb et al. [19], for instance, in a study of ammonia emission from gasoline-fuelled Euro-3 passenger cars with transient driving, have found that emissions of H_2 and NH_3 correlate during high velocity driving, as well as during acceleration events. Summers and Baron [20] in a study about the effects of SO_2 on NH_3 formation suggested that H_2 produced via SR and WGS reactions could be the major contributors to NH_3 formation.

It must be emphasized that reports from vehicles only describe emission rates as a function of the vehicle parameters and driving cycle. It is important to correlate the data reported from cars with that obtained from micro reactor studies in order to understand the reaction network during catalyst light-off or under equilibrium temperature operation.

3.2.2. *Model catalysts: Pd/Al_2O_3 and Pd/CeO_2–Al_2O_3*

To further understand the reactions involved during operation of TWC we also performed experiments with model catalysts. The formation of N_2O and NH_3 is observed in all cases studied, but there are differences depending on the support composition, primarily related to the presence of CeO_2. In the case of Pd/Al_2O_3 presented in Fig. 4, N_2O formation is activated already at 110 °C. The yield-temperature pattern in this case has a low temperature feature that might be caused by reaction of NO with H_2 in the feed (corresponds to H_2 emitted from the engine). After a local maximum at 170 °C there is a sharp increase in N_2O production reaching 600 ppm N_2O at 280 °C, presumably by reaction of NO with CO. N_2O ceases to be formed at 450 °C. The assignments are based on the fact that the complete conversion of H_2 at 180 °C in Fig. 4(a) coincides with the maximum production of N_2O presented in Fig. 4(b). On the other hand, the N_2O maximum at 280 °C in Fig. 4(b) correlates with

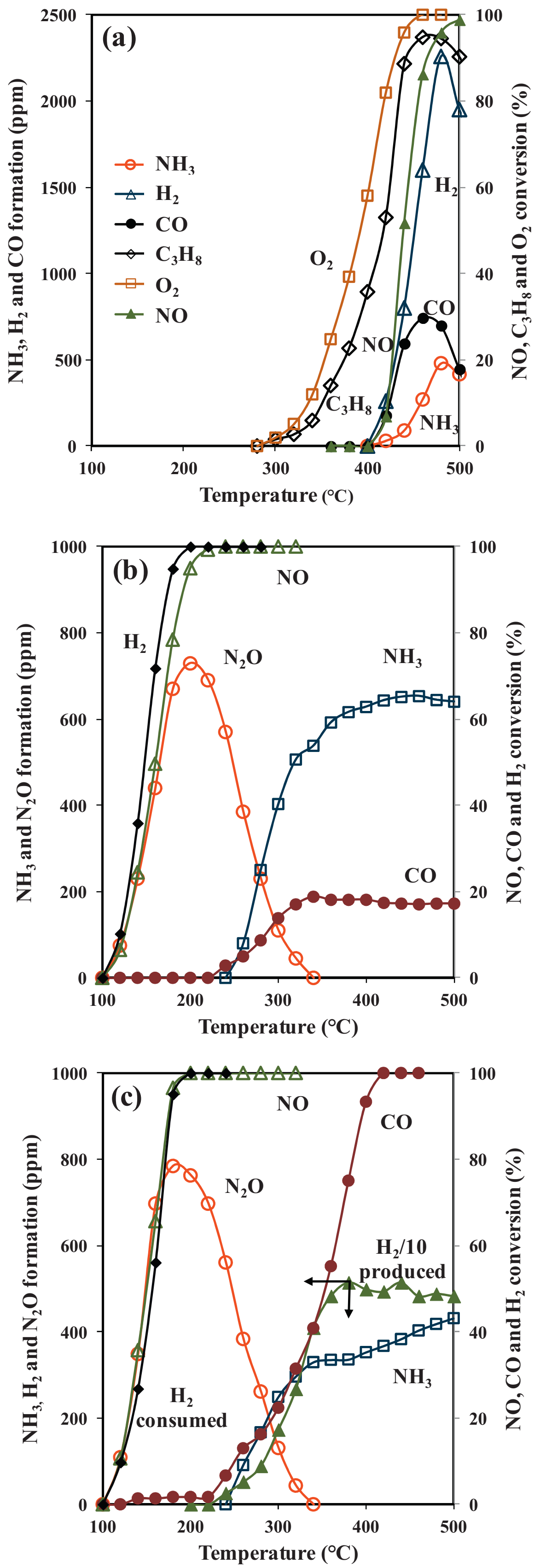

Fig. 2. N_2O, H_2 and NH_3 formation as a function of temperature over Pd-only TWC. (a) 2100 ppm of NO, 2250 ppm of C_3H_8 and 0.6% by volume of O_2, (b) 2100 ppm of NO, 2200 ppm of H_2 and 6600 ppm of CO and (c) 2100 ppm of NO, 2200 ppm of H_2, 6600 ppm of CO and 8% by volume of H_2O.

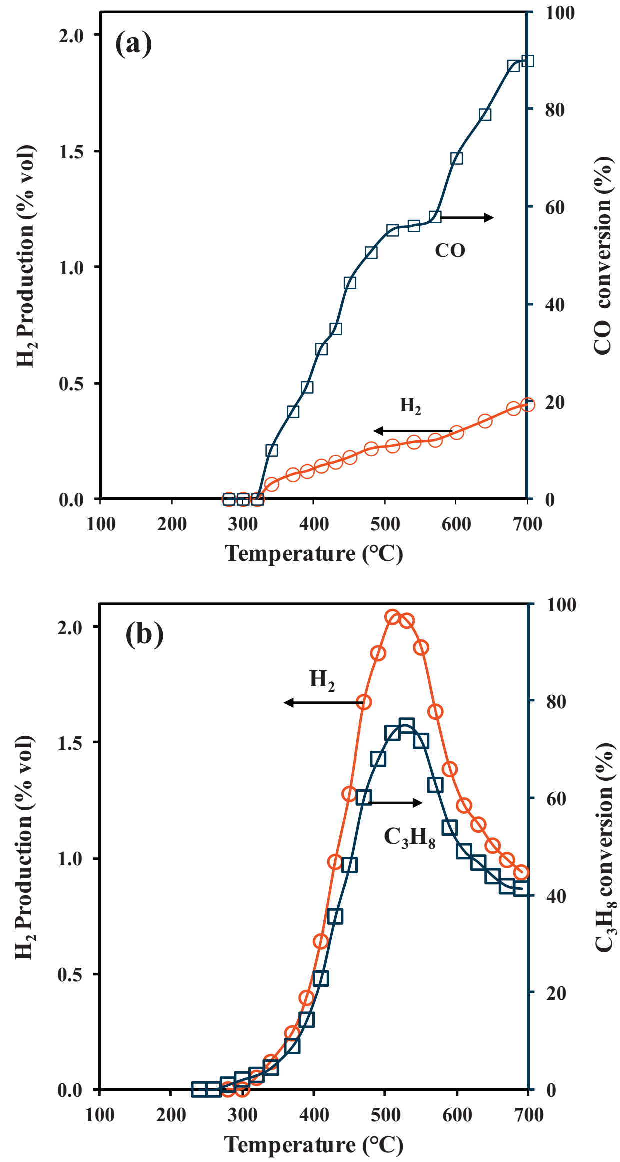

Fig. 3. (a) H_2 production via water gas-shift reaction and (b) steam reforming reaction over Pd-only TWC as a function of the temperature. Water was not monitored. The composition of the mixture of gases was 2250 ppm of C_3H_8 and 8% by vol. of H_2O for SR reaction. 5000 ppm of CO, 1700 ppm of H_2 and 8% by vol. of H_2O for WGS reaction. The space velocity, for both reactions, was 35,000 h^{-1}.

the conversion of CO shown in Fig. 4(a). During light-off, both H_2 and CO are also oxidized by molecular oxygen present in the feed stream to produce CO_2 and H_2O starting at 100 °C, see Fig. 4(a). All these reactions, reduction of NO by CO—H_2 and oxidation, are competitive.

Conversion of propane occurs only after CO has been consumed, i.e. above 250 °C, and it correlates with the formation of NH_3, shown in Fig. 4(a). As we show in a following section, the hydrogen required is formed via steam reforming in this case.

The behavior of the Pd/10-CeO_2–Al_2O_3 model catalyst (Fig. 5) is similar to that of the Pd-only TWC. There is a single N_2O peak, and the presence of ceria shifts about 80 °C the reduction of NO by CO to form N_2O towards lower temperature when compared with Pd/Al_2O_3, see Fig. 5(b). NH_3 is formed in a manner similar to the Pd-only TWC, starting at about 250 °C. At 400 °C the formation of NH_3 over Pd/10-CeO_2–Al_2O_3 (550 ppm) is larger than over Pd/Al_2O_3 (400 ppm).

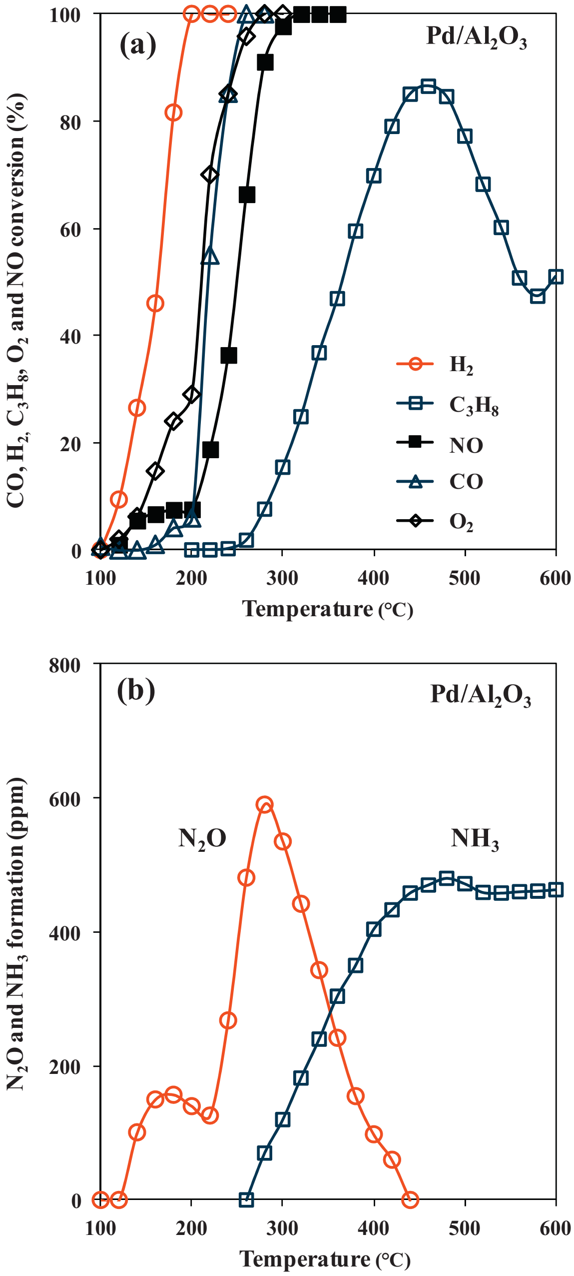

Fig. 4. (a) NO, CO, H_2, C_3H_8 and O_2 conversion as a function of the temperature and (b) N_2O and NH_3 formation over Pd/Al_2O_3 catalyst during light-off as a function of the temperature. Rich conditions – 2100 ppm of NO, 515 ppm of C_3H_8, 2200 ppm of H_2, 6600 ppm of CO, 10% (v/v) of H_2O and 0.53% by volume of O_2. A/F = 14.60.

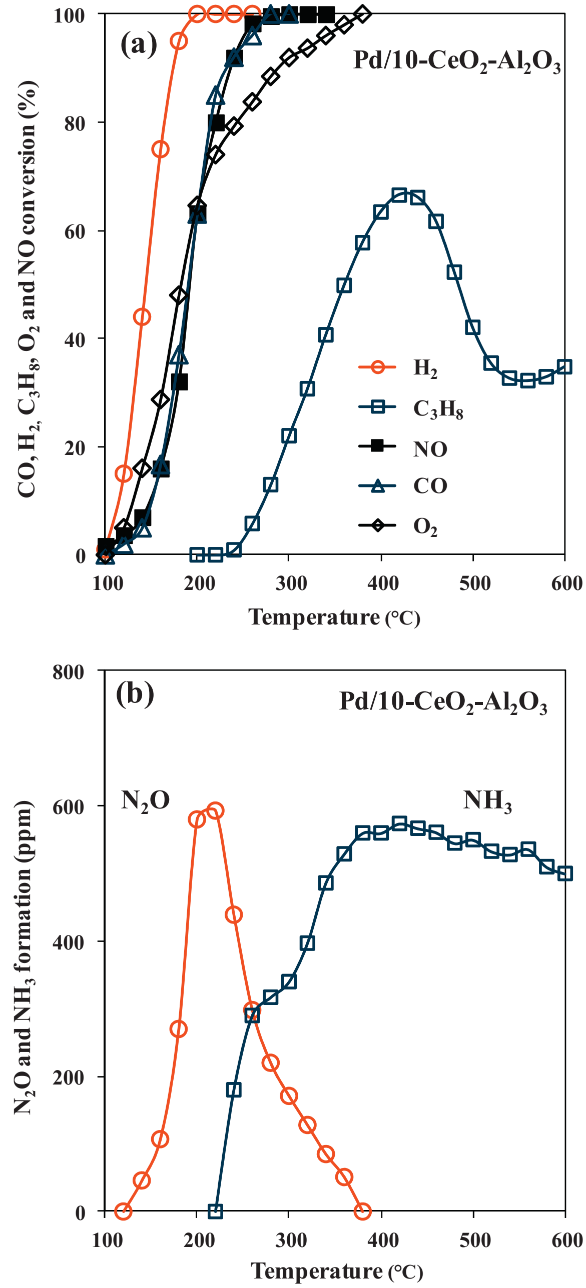

Fig. 5. (a) NO, CO, H_2, C_3H_8 and O_2 conversion as a function of the temperature and (b) N_2O and NH_3 formation over $Pd/10\text{-}CeO_2\text{–}Al_2O_3$ catalyst during light-off as a function of the temperature. Rich conditions – 2100 ppm NO, 515 ppm C_3H_8, 2200 ppm H_2, 6600 ppm CO, 10% (v/v) of H_2O and 0.53% volume by O_2. A/F = 14.60.

3.3. Steam reforming and water gas shift reactions on the TWC

Although it is commonly stated that SR and WGS reactions are responsible for the production of H_2 in cars [1,19,20], there are practically no reported results in the literature showing the production of H_2 with TWC. We performed SR and WGS reactions on the Pd-only TWC and model catalysts and determined that indeed those reactions occur to significant extent under conditions found in cars. The results are given in Fig. 6, and suggest that SR is the main source of H_2 between 300 and 500 °C. Above 500 °C, H_2 is also produced by WGS.

In our studies, production of H_2 by SR and WGS correlates with NH_3 formation. In all cases, the peak of maximum production of H_2, shown in Fig. 6, coincides with the largest formation of NH_3, shown in Figs. 1(b), 4(b) and 5(b). H_2 is produced mainly by SR reaction on Pd/Al_2O_3 catalyst between 320 and 550 °C. Pd/Al_2O_3 shows essentially no activity for WGS reaction. The low production of H_2 can explain the small amount of NH_3 reported in Fig. 4(b) for this catalyst. The presence of CeO_2, either in the case of Pd-only TWC or of $Pd/10\text{-}CeO_2\text{–}Al_2O_3$, enhances the generation of H_2 above 300 °C and hence the ensuing formation of NH_3 with those catalysts.

3.4. The effect of low sulfur level in gasoline: operation at constant temperature – 500 °C

Given the ongoing decrease in the level of sulfur in gasoline, it is important to understand what would be the impact on the NH_3 and N_2O formation at constant temperature, 500 °C. The temperature

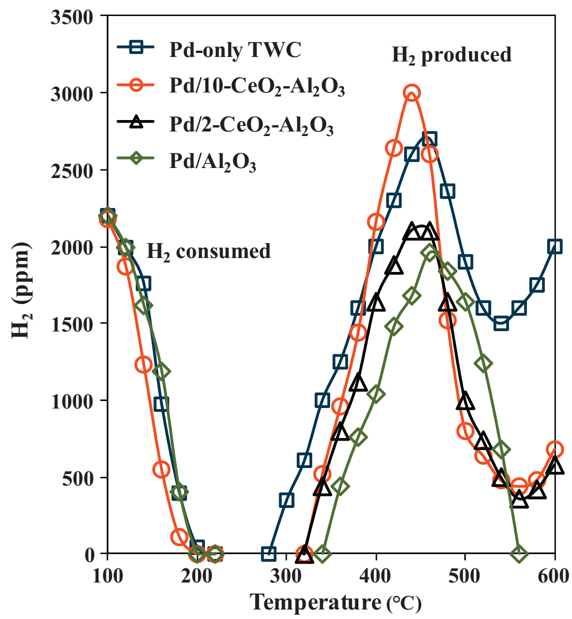

Fig. 6. H_2 production via steam reforming and water gas-shift reactions over Pd-only TWC (□), Pd/10-CeO_2–Al_2O_3 (○), Pd/2-CeO_2–Al_2O_3 (Δ) and Pd/Al_2O_3 (◊) catalysts as a function of the temperature. Rich conditions – 2100 ppm of NO, 515 ppm of C_3H_8, 2200 ppm of H_2, 6600 ppm of CO, 10% (v/v) of H_2O and 0.53% by volume of O_2. A/F = 14.60.

chosen corresponds roughly to the value reached when the velocity of the vehicle is close to 120 km/h, and represents the average TWC temperature during highway driving conditions [5,16].

We tested Pd-only TWC by varying SO_2 in the 0–50 ppm range under rich conditions. The results are given in Fig. 7. In the absence of SO_2, NH_3 is the main side-product. Once SO_2 is added to the feed stream the formation of NH_3 is inhibited, while there is now generation of N_2O. It is important to note that N_2O is produced during the constant temperature experiments at 500 °C, and its formation depends on the sulfur level. These results are an extension

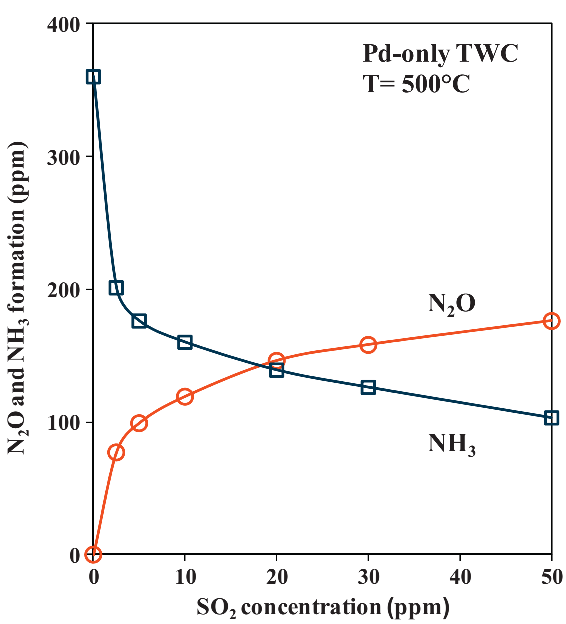

Fig. 7. Effect of the concentration of SO_2 upon NH_3 and N_2O formation. Commercial Pd-only TWC. Rich conditions – 2100 ppm of NO, 515 ppm of C_3H_8, 2200 ppm of H_2, 6600 ppm of CO, 10% (v/v) of H_2O and 0.53% by volume of O_2; SO_2 spanned 0–50 ppm. A/F = 14.60.

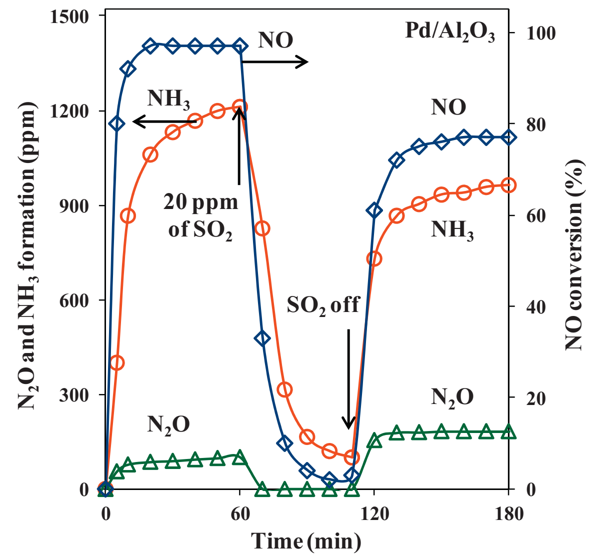

Fig. 8. Effect of 20 ppm of SO_2 upon NH_3 and N_2O formation and NO conversion over Pd/Al_2O_3 model catalyst. NO reduction by CO and H_2 at 500 °C – 2100 ppm of NO, 2200 ppm of H_2 and 6600 ppm of CO.

of the classic work of Gandhi and Shelef on sulfur poisoning of NH_3 formation over TWC under rich conditions [1].

To further understand the effect of the sulfur level upon the formation of side products over TWC, we performed a series of transient studies at 500 °C, shown in Fig. 8. Under sulfur-free conditions Pd/Al_2O_3 catalyzed the reduction of NO to N_2, NH_3 and N_2O. The addition of 20 ppm of SO_2 to the feed stream suppressed the activity of the catalyst almost completely. Once SO_2 was removed from the feed stream, the now sulfated Pd/Al_2O_3 showed a two-fold increase in N_2O formation, but both NO conversion and NH_3 production decreased compared to the fresh catalyst.

The presence of ceria in Pd/10-CeO_2–Al_2O_3 increases the selectivity towards NH_3, and decreases the formation of N_2O compared to Pd/Al_2O_3 in the absence of SO_2 in the feed, see Fig. 9. The addition of 20 ppm of SO_2 to the feed stream decreases the conversion of NO, but does not suppress it. After one hour of reaction in the presence of SO_2, the conversion of NO is almost 66% and the concentration

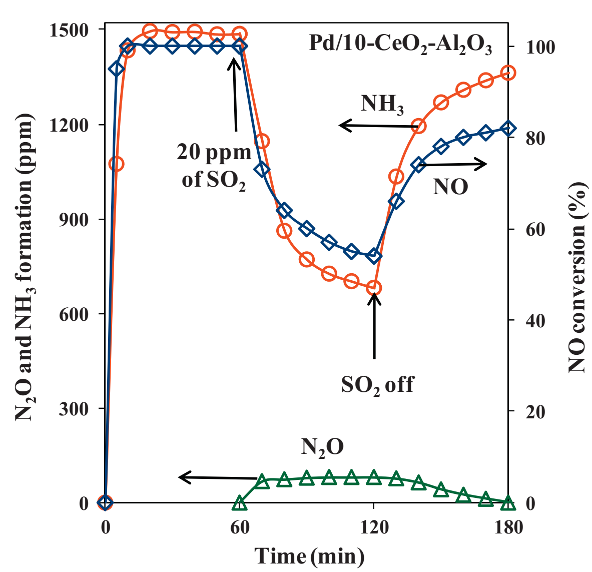

Fig. 9. Effect of 20 ppm of SO_2 upon NH_3 and N_2O formation and NO conversion over Pd/10-CeO_2–Al_2O_3 model catalyst during NO reduction by CO and H_2 at 500 °C. 2100 ppm of NO, 2200 ppm of H_2 and 6600 ppm of CO.

of NH_3 reaches 700 ppm. In agreement with our results using the TWC and simulated engine exhaust, see Fig. 7, the interaction of SO_2 with $Pd/CeO_2–Al_2O_3$ causes almost 100 ppm of N_2O to be formed at 500 °C. Once SO_2 is removed from the feed stream NO conversion and selectivity to NH_3 increase, whereas N_2O formation tampers off.

Our observations suggest that SO_2 affects both the support and the metal. On one hand, Al_2O_3 or $CeO_2–Al_2O_3$ are sulfated, presumably forming $Al_2(SO_4)_3$ and $Ce_2(SO_4)_3$ on the surface [21–23]. These structures are relatively stable, and affect the activity and selectivity of the catalysts once SO_2 is not present in the feed stream. The metal, Pd in this case, interacts with SO_2, presumably by chemisorption. This would explain the significant drop in activity in the presence of gaseous SO_2. These results are consistent with the well-known fact that presence of CeO_2 in TWC imparts sulfur resistance to these materials [1–7].

3.5. Formation of N_2O on TWC

The formation of N_2O at 500 °C over Pd-only TWC and supported Pd model catalysts as a function of the SO_2 concentration, or sulfur level in gasoline, has not been previously reported from cars, i.e., from TWC. This is the first report about N_2O formation on the TWC at high temperature operating under rich conditions. Our reaction conditions, temperature and air-to-fuel-ratio, as well as simulated exhaust gases, are qualitatively equivalent to those on the TWC when the vehicle is accelerated to 120 km/h [1,16,19], but the reason why the formation of N_2O on vehicles is not detected under the different driving cycles is not clear.

As it has been stated [24], there are limitations to the use of the FTIR spectroscopy in the measurement of N_2O concentrations in diluted exhaust samples and on-line-real-time analysis of N_2O from cars. One problem is the interference from CO absorption bands. The slow heating rate used in our study allowed us to analyze and quantify in more detail the spectra obtained by FTIR spectroscopy during light-off, and also during high temperature experiments. We were able to deconvolute readily the spectra to properly quantify the amount of N_2O.

Our results suggest that the actual urban inventories of N_2O could be underestimated because the contribution from the vehicular sector is not properly accounted for. Lower emissions of N_2O are expected from cars using low sulfur gasoline in the near future. However, the use of low sulfur gasoline by cars equipped with the Pd-only TWC promotes the formation of NH_3 and H_2, and an increase in the concentration of these compounds in the urban atmosphere is expected.

4. Conclusions

N_2O and NH_3 formation over Pd-only three way converters and supported Pd model catalysts occurs by NO reduction with either CO or H_2. N_2O is primarily formed during light-off (110–320 °C). We detected also formation of N_2O during operation at 500 °C under rich conditions. It is possible that N_2O emissions reported by in-use cars equipped with TWC could be underestimated, and so would be estimated urban N_2O inventories.

NH_3 is produced when the catalyst has reached its average operation temperature. We found that H_2 needed for its formation is produced by the SR and WGS reactions. On a molar basis, H_2 emission can be about 5-fold higher than that of NH_3.

The presence of SO_2 in the feed stream promotes the formation of N_2O but poisons that of NH_3. It also affects the conversion of NO, as is known. The addition of SO_2 affects TWC twofold, as it modifies the redox properties of ceria, through formation of sulfates, and probably oxysulfides, and it also affects Pd, probably by chemisorption.

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